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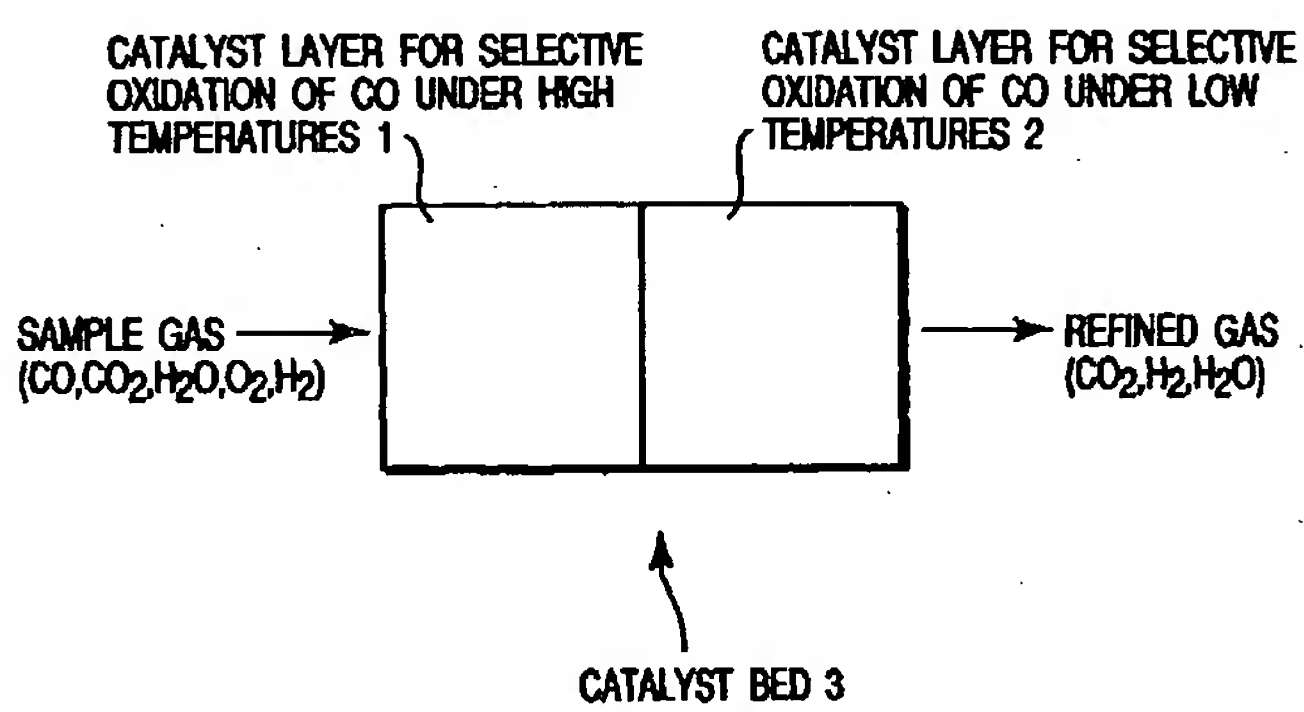
(54) Selective removing method of carbon monoxide

(57) According to the present invention, provided is a method of selectively removing carbon monoxide, comprising the steps of preparing a catalyst bed (3) capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers (1, 2) arranged in series and the plurality of catalyst layers (1, 2) differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer (1) having the highest application temperature constitutes the upstream side of the catalyst bed, and introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into the catalyst bed (3) through the upstream side of the catalyst bed (3) so as to selectively oxidize and remove CO from the gaseous mixture.



FIGURE

EP 1 059 263 A1

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Description

[0001] The present invention relates to a selective removing method of carbon monoxide.

[0002] A polymer electrolyte fuel cell permits suppressing generation of a pollutant causing an air pollution, is high in its heat efficiency and, thus, is expected to be used widely as a low temperature operation type fuel cell in a motor car power source, a dispersed power source or the like. A platinum catalyst is used mainly in the electrode of the polymer electrolyte fuel cell. Since the platinum catalyst tends to be poisoned by carbon monoxide (CO), it is necessary remove CO from the fuel gas as much as possible. The fuel gas is manufactured by, for example, reforming the fuel such as methanol by means of steam reforming reaction or a partial oxidation reaction so as to produce a hydrogen gas. Then, CO formed as a by-product in the hydrogen manufacturing reaction is removed by a CO shift reaction of

$$CO + H_2O \rightarrow CO_2 + H_2.$$

[0003] The removal of CO by the CO shift reaction is limited under the restriction in terms of the chemical equilibrium. For example, where a hydrogen gas is manufactured from methanol, followed by applying the CO shift reaction to the hydrogen-containing reaction mixture, the resultant gaseous composition contains about 40 to 60% of H_2, about 10% of CO_2, about 20% of H_2O, and about 0.5% of CO. It should be noted that, in order to prevent the polymer electrolyte fuel cell from being poisoned by CO, it is necessary to lower the CO concentration to 100 ppm or lower. Such being the situation, it is necessary to take measures for further lowering the CO concentration in combination with the CO shift reaction. As a particular measure, studied is a method in which an oxidizing agent of O_2 is added to the gaseous mixture after the CO shift reaction, followed by bringing the resultant gaseous mixture into contact with a catalyst capable of selectively oxidizing carbon monoxide so as to selectively oxidize CO within the gaseous mixture for removing CO.

[0004] However, the temperature at which the catalyst capable of selectively oxidizing carbon monoxide is allowed to perform its function sufficiently is limited. Therefore, if CO within the gaseous mixture is selectively oxidized in the presence of the catalyst, the carbon monoxide removal rate is fluctuated depending on the temperature of the gaseous mixture.

[0005] On the other hand, Japanese Patent Disclosure (Kokai) No. 6-296870 as claimed discloses a catalyst for cleaning the waste gas. It is taught that the catalyst consists of at least one metal selected from the platinum group elements, which is supported on a crystalline silicate having an X-ray diffraction pattern shown in Table A given in this prior art and represented in terms of the molar ratio of the oxide in a dehydrated state by a chemical formula $(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bM'O \cdot cAl_2O_3] \cdot ySiO_2$, where R denotes an alkali metal ion and/or hydrogen ion, M denotes an ion of at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, M' denotes an ion of alkaline earth metals of Mg, Ca, Sr, Ba, $0<a$, $0\leq b<20$, $a+c=1$, and $11<y<3000$.

[0006] This prior art also teaches in columns [0008] to [0009] that the particular waste gas cleaning catalyst permits cleaning the waste gas containing NO_x, CO and HC in accordance with reaction formulas (1) to (4) give below:

$$C_3H_6 + 3/2O_2 \rightarrow 3CH_2O \tag{1}$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{2}$$

$$CH_2O + 2NO \rightarrow N_2 + CO_2 + H_2O \tag{3}$$

$$CO + 1/2O_2 \rightarrow CO_2 \tag{4}$$

[0007] Reaction (1) given above represents activation of HC, reaction (2) represents combustion of HC, reaction (3) represents a denitrification, and reaction (4) represents combustion of CO.

[0008] An object of the present invention is to provide a method of selectively removing carbon monoxide that permits a high carbon monoxide removal rate over a wide temperature range in selectively removing CO from a gaseous mixture containing H_2 and CO.

[0009] According to a first aspect of the present invention, there is provided a method of selectively removing carbon monoxide, comprising the steps of:

preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and the plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and

introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into the catalyst bed through the

upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture.

[0010] According to a second aspect of the present invention, there is provided a method of selectively removing carbon monoxide, comprising the steps of:

preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and the plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and
introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into the catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture;
wherein the catalyst in each of the plurality of catalyst layers capable of selectively oxidizing carbon monoxide and differing from each other in the temperature of application includes at least one kind of a carrier and an active metal supported on the carrier, the carrier being selected from the group consisting of Y-type zeolite, mordenite, A-type zeolite, γ-Al_2O_3, anatase and a crystalline silicate having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \qquad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0\leq a$, $0\leq b\leq 20$, $a+c=1$, and $11\leq y\leq 3000$.

[0011] According to a third aspect of the present invention, there is provided a method of selectively removing carbon monoxide, comprising the steps of:

preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and the plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and
introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into the catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture;
wherein at least one kind of the catalyst includes a carrier and an active metal supported on the carrier, the carrier being a crystalline silicate having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \qquad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0\leq a$, $0\leq b\leq 20$, $a+c=1$, and $11\leq y\leq 3000$.

[0012] This summary of the invention does not necessarily describe all necessary features so that the invention may also be a sub-combination of these described features.

[0013] The invention can be more fully under stood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

[0014] The accompanying FIGURE schematically shows a catalyst bed used in Examples 1 to 23.

[0015] A method of the present invention for selectively removing carbon monoxide will now be described in detail.

[0016] The method of the present invention comprises the step of preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and the plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed, and the step of introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into the catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize CO and, thus, remove CO from the gaseous

mixture.

[0017] The oxygen gas (O_2) contained in the gaseous mixture is for oxidizing CO and, thus, need not be present together with H_2 and CO from the first. The method of the present invention comprises the step of adding an oxidizing agent of O_2 to a raw material gaseous mixture containing H_2 and CO, followed by introducing the resultant gaseous mixture into the catalyst bed. An oxygen gas or the air can be added to the raw material gaseous mixture.

[0018] The catalyst capable of selectively oxidizing carbon monoxide comprises a carrier and at least one kind of an active metal supported on the carrier. The catalyst capable of selectively oxidizing carbon monoxide can be used as it is in the form of a powder or can be held on a porous support.

[0019] The carrier used in the present invention is selected from the group consisting of Y-type zeolite, mordenite, A-type zeolite, γ-Al_2O_3, anatase-type TiO_2 and a crystalline silicate having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \qquad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0 \le a$, $0 \le b \le 20$, $a+c=1$, and $11 \le y \le 3000$.

[0020] The same carrier or a plurality of different carriers can be used for preparing a plurality of catalysts capable of selectively oxidizing carbon monoxide and differing from each other in the application temperature.

[0021] If the crystalline silicate fails to exhibit peaks at the five lattice spacing in the powder X-ray diffraction using a CuKα ray, or if the peaks, even if exhibited, fail to be any of the highest to the fifth highest peaks, it is impossible to selectively oxidize CO. It is desirable for the crystalline silicate to exhibit the highest to the fifth highest peaks in the powder X-ray diffraction using a CuKα ray at the five lattice spacing and to exhibit the sixth highest peak et seq. at the lattice spacing of 3.0±0.1Å, 3.3±0.1Å, 4.25±0.1Å, 5.6±0.2Å, 6.0±0.2Å, and 6.4±0.2Å. It is more desirable for the crystalline silicate to exhibit the highest to the eleventh highest peaks in the powder X-ray diffraction using a CuKα ray at the eleven lattice spacing and exhibit the twelfth highest peak et seq. at the lattice spacing of 3.05±0.1Å, 4.6±0.1Å, 5.7±0.2Å, and 6.7±0.2Å.

[0022] It is desirable to use the crystalline silicate among the carriers exemplified above.

[0023] The active metal supported on the carrier should be at least one kind of metal selected from the group consisting of Pt, Pd, Ru, Rh and Ir.

[0024] In selecting a plurality of catalysts differing from each other in the application temperature from among the catalysts capable of selectively oxidizing carbon monoxide, it is desirable to select a catalyst having Pt supported as an active metal on the carrier and another catalyst having at least one active metal selected from Pd, Ru, Rh and Ir supported on the carrier.

[0025] It is desirable for the CO concentration in the gaseous mixture containing H_2, O_2 and CO to be not higher than 4% when the gaseous mixture is introduced into the catalyst bed. If the CO concentration exceeds 4%, the reaction heat tends to be markedly elevated by the combustion heat generated by the combustion reaction of carbon monoxide, with the result that the selectivity of the catalyst capable of selectively oxidizing carbon monoxide tends to be lowered.

[0026] It is desirable to control the temperature of the gaseous mixture to fall within a range of between 50°C and 280°C when the gaseous mixture is introduced into the catalyst bed. If the temperature of the gaseous mixture is lower than 50°C, the selectivity of the catalyst capable of selectively oxidizing carbon monoxide tends to be markedly lowered. On the other hand, if the temperature of the gaseous mixture exceeds 280°C, the reaction rate of a side reaction of

$$2H_2 + O_2 \rightarrow 2H_2O$$

is increased. As a result, the oxidizing reaction of CO tends to be suppressed, resulting in failure to obtain a high CO removal rate.

[0027] According to the method of the present invention described above for selectively removing carbon monoxide, a plurality of catalysts capable of selectively oxidizing carbon monoxide and differing from each other in the application temperature are prepared and arranged in series in the order of the application temperature starting with the catalyst having the highest application temperature so as to form a catalyst bed. In the present invention, a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 is introduced into the catalyst bed through the catalyst layer having the highest application temperature. It should be noted that, where the gaseous mixture has a low temperature, the catalyst having the high application temperature, which is arranged in the upstream stage of the catalyst bed, scarcely performs its catalytic function. Where the gaseous mixture having a low temperature is introduced into the cat-

alyst layer having a low application temperature, which is arranged in the downstream stage of the catalyst bed, the catalyst vigorously performs the catalyst selectivity, thereby carbon monoxide is oxidized selectively. On the other hand, where a gaseous mixture having a high temperature is introduced into the catalyst bed, the catalyst having the high application temperature, which is arranged in the upstream stage, the catalyst vigorously performs the catalyst selectivity, thereby carbon monoxide is oxidized selectively. It follows that the catalysts having different application temperatures vigorously perform their catalytic functions depending on the temperature of the gaseous mixture containing CO and H_2, making it possible to process gaseous mixtures having a wide temperature range for selectively removing carbon monoxide with a high removal rate.

[0028] In the method of the present invention, it is desirable to use in combination a first catalyst capable of selectively oxidizing carbon monoxide, said first catalyst including a carrier and an active metal of Pt supported on the carrier, and a second catalyst capable of selectively oxidizing carbon monoxide, said second catalyst including a carrier and at least one kind of an active metal selected from Pd, Ru, Rh and Ir, said active metal being supported on the carrier. In this case, the application temperature of the first catalyst capable of selectively oxidizing carbon monoxide is lower than that of the second catalyst capable of selectively oxidizing carbon monoxide. As a result, a high CO removal rate can be achieved under a wide temperature range of the gaseous mixture, e.g., temperature range of between 50°C and 280°C.

[0029] In the present invention, it is particularly desirable to use a crystalline silicate having a composition represented by aforementioned formula (1) under a dehydrated state and having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, as a carrier of at least one of the first and second catalysts capable of selectively oxidizing carbon monoxide. In this case, it is possible to improve the carbon monoxide removal rate. The reasons for the improved carbon monoxide removal rate are considered to be as follows.

[0030] Specifically, the particular crystalline silicate specified in the present invention is hydrophobic so as to be unlikely to be affected by water that is present together, has a strong charge density distribution, and has fine pores sized about 6Å and, thus, adapted for the CO adsorption. As a result, the crystalline silicate specified in the present invention is capable of selectively adsorbing a polar substance of CO. It should also be noted that any of Pt, Pd, Ru, Rh and Ir supported on the crystalline silicate exhibits a high activity so as to adsorb O_2 contained in the gaseous mixture. As a result, CO adsorbed on the crystalline silicate can be preferentially oxidized by O_2 adsorbed on the active metal as denoted by reaction formula (A) given below, though side reactions (a) to (c) also take place to some extent so as to improve the selective oxidizing capability of the catalyst and, thus, to improve the carbon monoxide removal rate:

$$2CO + O_2 \rightarrow 2CO_2 \qquad \text{(A)}$$

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \text{(side reaction (a))}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(side reaction (b))}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{(side reaction (c))}$$

[0031] The method of the present invention can be used for refining a hydrogen-based fuel gas used in a polymer electrolyte fuel cell.

[0032] To be more specific, in order to obtain the fuel gas, a hydrogen gas is manufactured by applying a reforming reaction such as a steam reforming reaction or a partial oxidation reaction to methanol or hydrocarbons such as gasoline or methane. It should be noted that CO formed by a side reaction is contained in the reformed gas. Carbon monoxide contained in the reformed gas is removed in two stages. In the first stage, the CO concentration is lowered to a desired value by, for example, a CO shift reaction. Then, the residual CO is removed by the method of the present invention. To be more specific, the air or an oxygen gas is supplied to the gaseous material having the CO concentration lowered to a desired level. Also, a plurality of catalysts capable of selectively oxidizing carbon monoxide and differing from each other in the application temperature are prepared and arranged in the order of the application temperature such that the catalyst having a high application temperature is arranged in the front stage so as to form a catalyst bed. Then, the gaseous material having the CO concentration lowered to a desired level is introduced into the catalyst bed through the catalyst layer having a high application temperature. Since the catalyst having the application temperature adapted for the temperature of the introduced gas vigorously performs its catalytic function, it is possible to obtain a hydrogen-based fuel gas for a polymer electrolyte fuel cell having CO removed therefrom to a desired level, e.g., not higher than 100 ppm.

[0033] Some examples of the present invention will now be described in detail.

[0034] In the first step, honeycomb catalysts 1 to 24 used in the Examples of the present invention were prepared as follows.

Honeycomb Catalyst 1:

[0035] Water-glass No. 1 (SiO_2:30%) was dissolved in an amount of 5,616g in 5,429g of water to prepare solution A. On the other hand, dissolved in 4,175g of water were 18.9g of aluminum sulfate, 110g of ferric chloride, 47.2g of calcium acetate, 262g of sodium chloride, and 2,020g of a concentrated hydrochloric acid to prepare solution B. These solutions A and B were supplied at predetermined rates into a container to form precipitation, and the mixture was sufficiently stirred to obtain a slurry having a pH value of 8. The slurry was charged in an amount of 20 liters (L) into an autoclave, followed by introducing 500g of tetrapropyl ammonium bromide into the autoclave to carry out a hydrothermal synthesis at 160°C for 72 hours. After the synthesis, the reaction mixture was washed with water and, then, dried, followed by sintering the mixture at 500°C for 3 hours so as to obtain crystalline silicate 1 having a composition shown in Table 1 under a dehydrated state.

[0036] A powder X-ray diffraction measurement using CuKα ray was applied to the resultant crystalline silicate 1 to obtain the lattice spacing (d value) and relative intensities of the highest peak to the 15th highest peak, which are shown in Table 2.

[0037] As apparent from Table 2, the crystalline silicate 1 exhibited in the powder X-ray diffraction using a CuKα ray the highest to the fifth highest peaks at the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, the sixth highest to the eleventh highest peaks at the lattice spacing of 3.0±0.1Å, 3.3±0.1Å, 4.25±0.1Å, 5.6±0.2Å, 6.0±0.2Å, and 6.4±0.2Å, respectively, and the twelfth highest to the fifteenth highest peaks at the lattice spacing of 3.05±0.1Å, 4.6±0.1Å, 5.7±0.2Å, and 6.7±0.2Å, respectively.

[0038] The crystalline silicate 1 was dipped in a 4N NH_4Cl aqueous solution maintained at 40°C and the solution was kept stirred for 3 hours so as to carry out the NH_4 ion exchange. After the ion exchange, the crystalline silicate 1 was washed and, then, dried at 100°C for 24 hours, followed by sintering the crystalline silicate at 400°C for 3 hours so as to obtain the H-type crystalline silicate 1.

[0039] Then, 100 parts of the H-type crystalline silicate 1 was impregnated with an aqueous solution of chloroplatinic acid (H_2PtCl_6) to permit 0.4 part by weight of platinum to be supported by the crystalline silicate 1, followed by evaporating the solvent for the drying purpose and subsequently performing sintering at 500°C for 5 hours so as to obtain a powdery catalyst.

[0040] A binder consisting of 3 parts of alumina sol (Al_2O_3:10%) and 55 parts of silica sol (SiO_2: 20 parts) was added to the resultant powdery catalyst together with 200 parts of water, and the aqueous system was sufficiently stirred to prepare a slurry for wash coating. Then, a monolithic substrate made of cordierite ceramics and having 400 cell lattice meshes was dipped in the slurry. After the substrate was taken out of the slurry, the slurry attached to the substrate was blown off, followed by drying the substrate at 200°C. The coating amount was 150g per liter of the monolithic substrate, and the coated substrate constituted the honeycomb catalyst 1.

Honeycomb Catalysts 2 to 12:

[0041] Crystalline silicates 2 to 12 having the compositions as shown in Table 1 under a dehydrated state were prepared as in preparation of honeycomb catalyst 1 described above, except that cobalt chloride, ruthenium chloride, rhodium chloride, lanthanum chloride, cerium chloride, titanium chloride, vanadium chloride, chromium chloride, antimony chloride, gallium chloride and niobium chloride were added in place of ferric chloride used in preparation of honeycomb catalyst 1 in a molar amount equal to Fe_2O_3 in terms of oxides.

[0042] A powder X-ray diffraction measurement using a CuKα ray was applied to each of these crystalline silicates 2 to 12, finding that the lattice spacing and the relative intensities of the highest to the fifteenth highest peaks were as shown in Table 2.

[0043] Then, honeycomb catalysts 2 to 12 were prepared as in preparation of honeycomb catalyst 1 described above.

Honeycomb Catalysts 13 to 15:

[0044] Crystalline silicates 13 to 15 having the compositions as shown in Table 1 under a dehydrated state were prepared as in preparation of honeycomb catalyst 1 described above, except that magnesium acetate, strontium acetate and barium acetate were added in place of calcium acetate used in preparation of honeycomb catalyst 1 in a molar amount equal to CaO in terms of oxides.

[0045] A powder X-ray diffraction measurement using a CuKα ray was applied to each of these crystalline silicates 13 to 15, finding that the lattice spacing and the relative intensities of the highest to the fifteenth highest peaks were as shown in Table 2.

[0046] Then, honeycomb catalysts 13 to 15 were prepared as in preparation of honeycomb catalyst 1 described above.

Honeycomb Catalyst 16:

[0047] A carrier consisting of 100 parts of an H-type crystalline silicate 1 equal to that described previously in conjunction with honeycomb catalyst 1 described previously was impregnated with an aqueous solution of palladium chloride to permit 0.4 part by weight of Pd to be supported by the carrier, followed by evaporating the solution and drying the carrier impregnated with palladium and subsequently sintering the carrier at 500°C for 5 hours so as to obtain powdery catalyst. Further, a honeycomb catalyst 16 was prepared from the powdery catalyst by the method equal to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 17:

[0048] A carrier consisting of 100 parts of an H-type crystalline silicate 1 equal to that described previously in conjunction with honeycomb catalyst 1 described previously was impregnated with an aqueous solution of rhodium chloride to permit 0.4 part by weight of Rh to be supported by the carrier, followed by evaporating the solution and drying the carrier impregnated with rhodium and subsequently sintering the carrier at 500°C for 5 hours so as to obtain powdery catalyst. Further, a honeycomb catalyst 17 was prepared from the powdery catalyst by the method equal to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 18:

[0049] A carrier consisting of 100 parts of an H-type crystalline silicate 1 equal to that described previously in conjunction with honeycomb catalyst 1 described previously was impregnated with an aqueous solution of ruthenium chloride to permit 0.4 part by weight of Ru to be supported by the carrier, followed by evaporating the solution and drying the carrier impregnated with ruthenium and subsequently sintering the carrier at 500°C for 5 hours so as to obtain powdery catalyst. Further, a honeycomb catalyst 18 was prepared from the powdery catalyst by the method equal to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 19:

[0050] A carrier consisting of 100 parts of an H-type crystalline silicate 1 equal to that described previously in conjunction with honeycomb catalyst 1 described previously was impregnated with an aqueous solution of iridium chloride to permit 0.4 part by weight of Ir to be supported by the carrier, followed by evaporating the solution and drying the carrier impregnated with rhodium and subsequently sintering the carrier at 500°C for 5 hours so as to obtain powdery catalyst. Further, a honeycomb catalyst 19 was prepared from the powdery catalyst by the method equal to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 20:

[0051] A powdery catalyst was prepared by impregnating an H-type Y-zeolite powder with an aqueous solution of chloroplatinic acid to permit 0.4 part by weight of Pt to be supported by the zeolite powder. Then, a honeycomb catalyst 20 was prepared by the method similar to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 21:

[0052] A powdery catalyst was prepared by impregnating an H-type mordenite powder with an aqueous solution of chloroplatinic acid to permit 0.4 part by weight of Pt to be supported by the mordenite powder. Then, a honeycomb catalyst 21 was prepared by the method similar to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 22:

[0053] A powdery catalyst was prepared by impregnating an Ca-type A-zeolite powder with an aqueous solution of chloroplatinic acid to permit 0.4 part by weight of Pt to be supported by the zeolite powder. Then, a honeycomb catalyst 22 was prepared by the method similar to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 23:

[0054] A powdery catalyst was prepared by impregnating a γ-Al_2O_3 powder with an aqueous solution of chloroplatinic acid to permit 0.4 part by weight of Pt to be supported by the alumina powder. Then, a honeycomb catalyst 23 was prepared by the method similar to that described previously in conjunction with preparation of honeycomb catalyst 1.

Honeycomb Catalyst 24:

[0055] A powdery catalyst was prepared by impregnating an anatase-type TiO_2 powder with an aqueous solution of chloroplatinic acid to permit 0.4 part by weight of Pt to be supported by the TiO_2 powder. Then, a honeycomb catalyst 24 was prepared by the method similar to that described previously in conjunction with preparation of honeycomb catalyst 1.

[0056] Table 1 shows compositions of the crystalline silicate or carrier and the metals supported on the carriers in respect of the honeycomb catalysts 1 to 24 thus prepared:

Table 1

Honeycomb catalyst No.	Active metal	Carrier No.	Composition of crystalline silicate or carrier
1	Pt	1	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0 \cdot 8Al_2O_3 \cdot 0.2CaO]25SiO_2$
2	Pt	2	$0.5Na_2O \cdot 0.5H_2O[0.2Co_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
3	Pt	3	$0.5Na_2O \cdot 0.5H_2O[0.2Ru_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
4	Pt	4	$0.5Na_2O \cdot 0.5H_2O[0.2Rh_2O_3 \cdot 0.8Al_2O_3.0.2CaO]25SiO_2$
5	Pt	5	$0.5Na_2O \cdot 0.5H_2O[0.2La_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
6	Pt	6	$0.5Na_2O \cdot 0.5H_2O[0.2Ce_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
7	Pt	7	$0.5Na_2O \cdot 0.5H_2O[0.2Ti_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
8	Pt	8	$0.5Na_2O \cdot 0.5H_2O[0.2V_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
9	Pt	9	$0.5Na_2O \cdot 0.5H_2O[0.2Cr_2O_3 \cdot 0.8Al_2O_30.2CaO]25SiO_2$
10	Pt	10	$0.5Na_2O \cdot 0.5H_2O[0.2Sb_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
11	Pt	11	$0.5Na_2O \cdot 0.5H_2O[0.2Ga_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
12	Pt	12	$0.5Na_2O \cdot 0.5H_2O[0.2Nb_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
13	Pt	13	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2MgO]25SiO_2$
14	Pt	14	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2SrO]25SiO_2$
15	Pt	15	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2BaO]25SiO_2$
16	Pd	1	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
17	Rh	1	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
18	Ru	1	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
19	Ir	1	$0.5Na_2O \cdot 0.5H_2O[0.2Fe_2O_3 \cdot 0.8Al_2O_3 \cdot 0.2CaO]25SiO_2$
20	Pt	16	Y-type zeolite (molar ratio of SiO_2 to Al_2O_3 being 5.2)
21	Pt	17	Mordenite (molar ratio of SiO_2 to Al_2O_3 being 10)
22	Pt	18	A-type zeolite (molar ratio of SiO_2 to Al_2O_3 being 0.5)
23	Pt	19	γ-Al_2O_3
24	Pt	20	Anatase type TiO_2

Table 2

Lattice spacing (d value)	Relative intensity
11.2±0.3	VS
10.0±0.3	VS
6.7±0.2	W
6.4±0.2	M
6.0±0.2	M
5.7±0.2	W
5.6±0.2	M
4.6±0.1	W
4.25±0.1	M
3.85±0.1	VS
3.75±0.1	S
3.65±0.1	S
3.3±0.1	M
3.05±0.1	W
3.0±0.1	M
VS : very strong S : strong M : medium W : weak X-ray source : CuKα	

Examples 1 to 23:

[0057] A single kind of honeycomb catalyst 1 for selective CO oxidation at a low temperature having an application temperature falling within a range of between 50°C and 150°C and another honeycomb catalyst 2 having an application temperature higher than the application temperature for the low temperature CO oxidation catalyst, said application temperature falling within a range of between 150°C and 270°C, were selected from among the honeycomb catalysts 1 to 24. These CO selective oxidation catalyst 1 for high temperatures and CO selective oxidation catalyst 2 for low temperatures were arranged in series to form 23 kinds of a catalyst bed 3, as shown in the accompanying Figure. Tables 3 and 4 show the kinds of the honeycomb catalysts constituting each of these catalyst beds. Each of these CO selective oxidation catalysts 1 and 2 for high and low temperatures, respectively, was loaded in the catalyst bed in an amount of 15 cc, totaling 30 cc of the catalysts 1 and 2.

[0058] A sample gas containing 0.6% of CO, 24% of CO_2, 20% of H_2O, 0.6% of O_2 and 54.8% of H_2 and having a temperature of 70°C was introduced into the catalyst bed 3 through the catalyst layer 1 of a high application temperature with GHSV (gas hourly space velocity) set at 10,000 h^{-1} (gas amount of 300 NL/h) so as to remove carbon monoxide from the sample gas. During the test, the CO concentration at the outlet port of the catalyst bed 3 was continuously monitored by a ND-IR type CO meter and the CO concentration was measured when the CO concentration was stabilized. Tables 3 and 4 show the results. The particular CO removal test was conducted with the temperature of the sample gas changed to 100°C, 130°C, 160°C, 190°C, 220°C and 270°C. The results are also shown in Tables 3 and 4.

Comparative Examples 1 to 5:

[0059] One kind of a catalyst was selected from among the honeycomb catalysts 1 to 24 and the catalyst thus selected was used both as catalysts 1 and 2. The amount of each of these catalysts 1 and 2 was 15 cc, totaling 30 cc of catalysts 1 and 2. These catalysts 1 and 2 were arranged as shown in the FIGURE to form the catalyst bed 3. A sam-

ple gas having the composition equal to that of the sample gas used in Examples 1-23 and a temperature of 70°C was introduced into the catalyst bed 3 through the catalyst layer 1 of a high application temperature with GHSV (gas hourly space velocity) set at 10,000 h^{-1} (gas amount of 300 NL/h) so as to remove carbon monoxide from the sample gas. During the test, the CO concentration at the outlet port of the catalyst bed 3 was continuously monitored by a ND-IR type CO meter and the CO concentration was measured when the CO concentration was stabilized. Table 4 shows the results. The particular CO removal test was conducted with the temperature of the sample gas changed to 100°C, 130°C, 160°C, 190°C, 220°C and 270°C. The results are also shown in Table 4.

Table 3

	Honeycomb catalyst for high temperature (metal)	Honeycomb catalyst for low temperature (metal)	CO concentration at outlet of catalyst bed at various temperature of sample gas (ppm)						
			70°C	100°C	130°C	160°C	190°C	220°C	270°C
Example 1	18 (Ru)	1 (Pt)	28	15	8	19	32	39	55
Example 2	18 (Ru)	2 (Pt)	26	13	7	15	29	39	47
Example 3	18 (Ru)	3 (Pt)	23	11	6	13	33	41	45
Example 4	18 (Ru)	4 (Pt)	20	12	8	12	35	42	50
Example 5	18 (Ru)	5 (Pt)	23	11	9	16	34	35	48
Example 6	18 (Ru)	6 (Pt)	29	13	7	15	33	36	65
Example 7	18 (Ru)	7 (Pt)	22	11	8	14	32	34	49
Example 8	18 (Ru)	8 (Pt)	23	10	7	13	33	35	47
Example 9	18 (Ru)	9 (Pt)	21	12	7	14	32	39	50
Example 10	18 (Ru)	10 (Pt)	20	9	10	14	29	38	45
Example 11	18 (Ru)	11 (Pt)	29	14	8	15	29	35	52
Example 12	18 (Ru)	12 (Pt)	22	14	8	19	33	40	45
Example 13	18 (Ru)	13 (Ir)	29	15	8	16	32	39	46
Example 14	18 (Ru)	14 (Ru)	23	16	12	18	33	40	55

Table 4

	Honeycomb catalyst for high temperature (metal)	Honeycomb catalyst for low temperature (metal)	CO concentration at outlet of catalyst bed at various temperature of sample gas (ppm)						
			70°C	100°C	130°C	160°C	190°C	220°C	270°C
Example 15	18 (Ru)	15 (Pt)	22	14	13	19	38	41	48
Example 16	16 (Rd)	1 (Pt)	25	16	14	28	34	42	120
Example 17	17 (Rh)	1 (Pt)	24	25	19	15	25	100	130
Example 18	19 (Ir)	1 (Pt)	45	29	13	10	20	54	72
Example 19	18 (Ru)	20 (Pt)	76	46	34	20	37	45	53
Example 20	18 (Ru)	21 (Pt)	69	50	25	23	34	44	56
Example 21	18 (Ru)	22 (Pt)	70	45	23	20	34	42	51

Table 4 (continued)

	Honeycomb catalyst for high temperature (metal)	Honeycomb catalyst for low temperature (metal)	CO concentration at outlet of catalyst bed at various temperature of sample gas (ppm)						
			70°C	100°C	130°C	160°C	190°C	220°C	270°C
Example 22	18 (Ru)	23 (Pt)	69	50	19	21	33	45	55
Example 23	18 (Ru)	24 (Pt)	70	30	12	10	18	36	50
Comparative Example 1	1 (Pt)	1 (Pt)	34	10	15	34	70	450	1800
Comparative Example 2	21 (Pt)	21 (Pt)	55	42	22	33	100	560	3200
Comparative Example 3	22 (Pt)	22 (Pt)	70	55	30	23	160	1000	3300
Comparative Example 4	19 (Ir)	19 (Ir)	380	220	130	130	120	80	60
Comparative Example 5	18 (Ru)	18 (Ru)	3400	2200	1900	1700	140	45	41

[0060] As apparent from Tables 3 and 4, in Examples 1 to 23, in which two kinds of catalysts 1 and 2 differing from each other in the application temperature were arranged such that the catalyst layer 1 having a high application temperature was arranged on the upstream side and a sample gas containing H_2, O_2 and CO was passed through the catalyst bed 3 from the catalyst layer 1 having a high application temperature, it was possible to lower the CO concentration in the sample gas over a wide temperature range of 70 to 270°C at the sample gas. However, in Comparative Examples 1 to 3, in which the catalyst layers 1 and 2 of the catalyst bed 3 were formed of the same catalyst having Pt supported as an active metal on the carrier, the CO concentration at the outlet of the catalyst bed 3 in the case where the temperature of the sample gas was 190 to 270°C was found to be higher than in the case where the temperature of the sample gas was 70 to 160°C. On the other hand, in Comparative Examples 4 and 5, in which the catalyst layers 1 and 2 of the catalyst bed 3 were formed of the same catalyst having Ir or Ru supported as an active metal on the carrier, the CO concentration at the outlet of the catalyst bed 3 in the case where the temperature of the sample gas was 70 to 160°C was found to be higher than in the case where the temperature of the sample gas was 190 to 270°C.

Examples 24 to 27:

[0061] Three kinds of catalysts differing from each other in the application temperature were selected from among the honeycomb catalysts 1 to 24 and arranged in series in the order of the application temperature such that the honeycomb catalyst having a high application temperature was arranged on the upstream side so as to form the catalyst bed 3. The amount of each of these three catalysts was 15 cc, totaling 45 cc of the catalysts. Four different kinds of the catalyst bed were prepared.

[0062] A sample gas having the composition equal to that of the sample gas used in Examples 1-23 and having a temperature of 60°C was introduced into the catalyst bed 3 through the catalyst layer of a high application temperature with GHSV (gas hourly space velocity) set at 10,000 h^{-1} (gas amount of 450 NL/h) so as to remove carbon monoxide from the sample gas. During the test, the CO concentration at the outlet port of the catalyst bed 3 was continuously monitored by a ND-IR type CO meter and the CO concentration was measured when the CO concentration was stabilized. Table 5 shows the results. The particular CO removal test was conducted with the temperature of the sample gas changed to 120°C, 200°C and 280°C. The results are also shown in Table 5.

Table 5

	Honeycomb catalyst for high temperature (metal)	Honeycomb catalyst for intermediate temperature (metal)	Honeycomb catalyst for low temperature (metal)	CO concentration at outlet of catalyst bed at various temperature of sample gas (ppm)			
				60°C	120°C	200°C	280°C
Example 24	18 (Ru)	19 (Ir)	1 (Pt)	12	15	23	29
Example 25	18 (Ru)	19 (Ir)	20 (Pt)	42	48	34	25
Example 26	18 (Ru)	17 (Rh)	1 (Pt)	13	16	37	38
Example 27	19 (Ir)	17 (Rh)	1 (Pt)	14	19	45	80

[0063] As apparent from Table 5, in Examples 24 to 27, in which three kinds of catalysts differing from each other in the application temperature were arranged in series in the order of the application temperature such that the catalyst having a high application temperature was arranged on the upstream side so as to form the catalyst bed and a sample gas containing H_2, CO and an oxidizing gas of O_2 was passed through the catalyst bed from the catalyst layer having a high application temperature, the temperature range in which a high CO removal rate can be obtained can be widened to 60 to 280°C, compared with the range of between 70°C and 270°C for Examples 1 to 23.

[0064] In the Examples described above, the crystalline silicate carrier of the catalyst capable of selectively oxidizing carbon monoxide was of H-type. However, it has also been confirmed that it is possible to obtain the similar effects in the case of using a catalyst capable of selectively oxidizing carbon monoxide, said catalyst having a crystalline silicate carrier represented by formula (1) in a dehydrated state in which R represents an alkali metal or a composition of an alkali metal and proton..

[0065] Also, in the Examples described above, the catalyst bed was prepared by arranging in series two or three kinds of catalysts capable of selectively oxidizing carbon monoxide. If four or more kinds catalysts are arranged in series to form a catalyst bed, the carbon monoxide removal rate can be further increased, and the temperature range in which a high carbon monoxide removal rate can be obtained can be further widened.

[0066] As described above in detail, the present invention provides a method of selectively removing carbon monoxide from a gaseous mixture containing H_2 and CO, which permits a high carbon monoxide removal rate over a wide temperature range.

Claims

1. A method of selectively removing carbon monoxide, comprising the steps of:

   preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and said plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and
   introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into said catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture.

2. The method of selectively removing carbon monoxide according to claim 1, characterized in that said plurality of catalysts capable of selectively oxidizing carbon monoxide and differing from each other in the application temperature comprises a first catalyst for selectively oxidizing carbon monoxide, said first catalyst including a carrier and Pt acting as an active metal and supported on said carrier, and a second catalyst for selectively oxidizing carbon monoxide, said second catalyst including a carrier and an active metal consisting of at least one kind of metal selected from the group consisting of Pd, Ru, Rh and Ir and supported on said carrier.

3. The method of selectively removing carbon monoxide according to claim 2, characterized in that said carrier of said first and second catalysts for selectively oxidizing carbon monoxide is selected from the group consisting of Y-type zeolite, mordenite, A-type zeolite, γ-Al_2O_3, anatase and a crystalline silicate having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehy-

drated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \quad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0\leq a$, $0\leq b\leq 20$, $a+c=1$, and $11\leq y\leq 3000$.

4. The method of selectively removing carbon monoxide according to claim 1, characterized in that each of said plurality of catalysts capable of selectively oxidizing carbon monoxide and differing from each other in the application temperature is formed of a catalyst including a carrier and an active metal consisting of at least one kind of metal selected from the group consisting of Pd, Ru, Rh and Ir and supported on said carrier.

5. The method of selectively removing carbon monoxide according to claim 4, characterized in that said carrier is selected from the group consisting of Y-type zeolite, mordenite, A-type zeolite, γ-Al_2O_3, anatase and a crystalline silicate having the highest to fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \quad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0\leq a$, $0\leq b\leq 20$, $a+c=1$, and $11\leq y\leq 3000$.

6. The method of selectively removing carbon monoxide according to claim 1, characterized in that the temperature of said gaseous mixture falls within a range of between 50°C and 280°C when said gaseous mixture is introduced into said catalyst bed.

7. The method of selectively removing carbon monoxide according to claim 1, characterized in that the CO concentration of said gaseous mixture is not higher than 4%.

8. A method of selectively removing carbon monoxide, comprising the steps of:

preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and said plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and
introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into said catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture;
wherein the catalyst in each of said plurality of catalyst layers capable of selectively oxidizing carbon monoxide and differing from each other in the temperature of application includes at least one kind of a carrier and an active metal supported on said carrier, said carrier being selected from the group consisting of Y-type zeolite, mordenite, A-type zeolite, γ-Al_2O_3, anatase and a crystalline silicate having the highest to the fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \quad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0\leq a$, $0\leq b\leq 20$, $a+c=1$, and $11\leq y\leq 3000$.

9. The method of selectively removing carbon monoxide according to claim 8, characterized in that said active metal

consists of at least one metal selected from the group consisting of Pt, Pd, Ru, Rh and Ir.

10. The method of selectively removing carbon monoxide according to claim 8, characterized in that the temperature of said gaseous mixture falls within a range of between 50°C and 280°C when said gaseous mixture is introduced into said catalyst bed.

11. The method of selectively removing carbon monoxide according to claim 8, characterized in that the CO concentration of said gaseous mixture is not higher than 4%.

12. A method of selectively removing carbon monoxide, comprising the steps of:

preparing a catalyst bed capable of selectively oxidizing carbon monoxide and including a plurality of catalyst layers arranged in series and said plurality of catalyst layers differing from each other in the temperature of application and arranged in the order of the application temperature such that the catalyst layer having the highest application temperature constitutes the upstream side of the catalyst bed; and

introducing a gaseous mixture containing H_2, CO and an oxidizing agent of O_2 into said catalyst bed through the upstream side of the catalyst bed so as to selectively oxidize and remove CO from the gaseous mixture;

wherein at least one kind of the catalyst includes a carrier and an active metal supported on said carrier, said carrier being a crystalline silicate having the highest to fifth highest peaks in the powder X-ray diffraction using CuKα ray in the lattice spacing of 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 10.0±0.3Å, and 11.2±0.3Å, respectively, and having the composition represented by formula (1) under a dehydrated state:

$$(1\pm0.8)R_2O \cdot [aM_2O_3 \cdot bNO \cdot cAl_2O_3] \cdot ySiO_2 \quad (1)$$

where R denotes at least one element selected from the group consisting of an alkali metal and H, M denotes at least one element selected from the group consisting of VIII group elements, rare earth elements, Ti, V, Cr, Nb, Sb and Ga, N denotes at least one element selected from the group consisting of Mg, Ca, Sr, and Ba, and the molar ratios a, b, c and y are: $0 \leq a$, $0 \leq b \leq 20$, $a+c=1$, and $11 \leq y \leq 3000$.

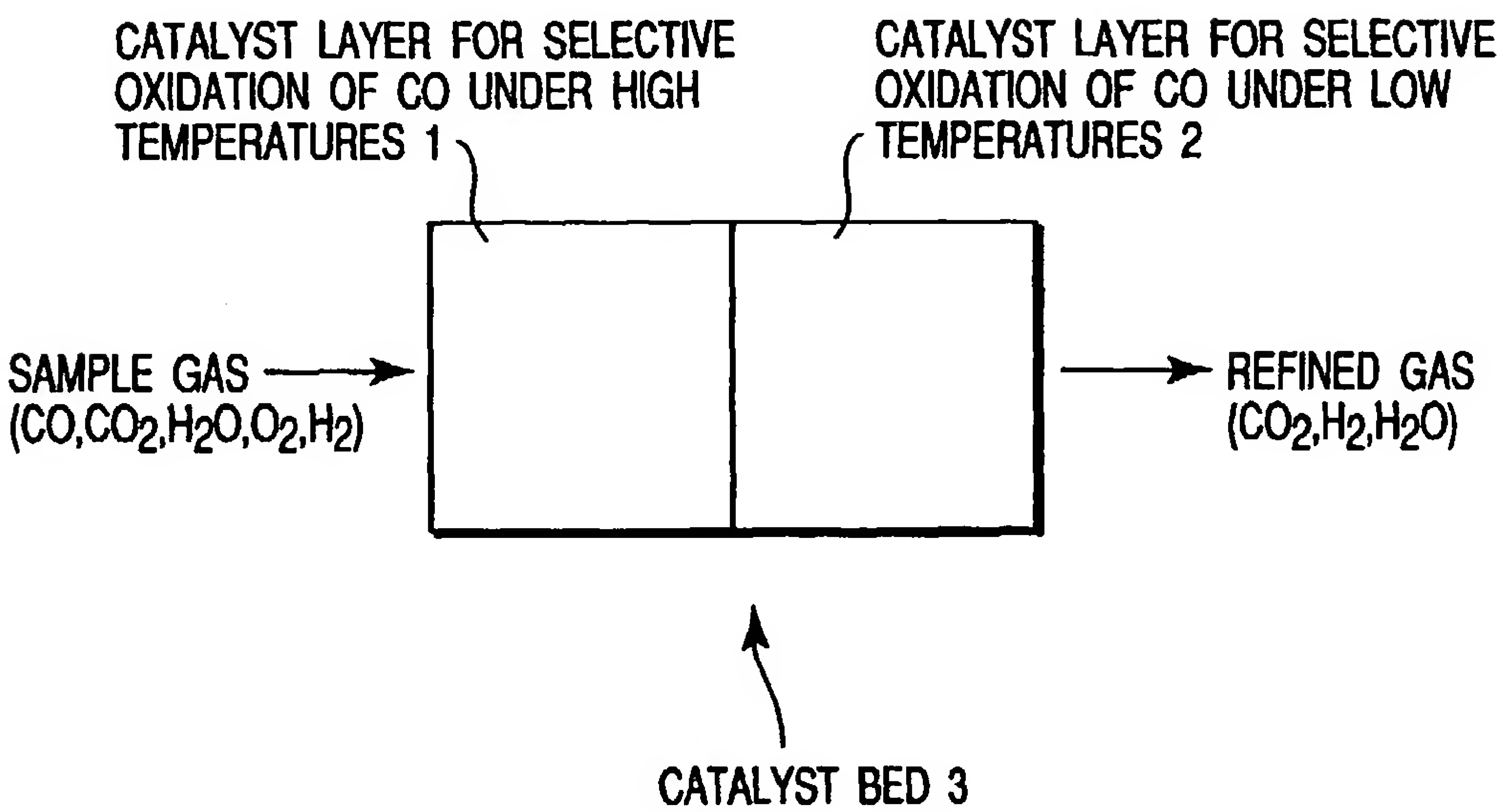
13. The method of selectively removing carbon monoxide according to claim 12, characterized in that said crystalline silicate exhibits the highest to the eleventh highest peaks in a powder X-ray diffraction using a CuKα ray in the lattice spacing of 3.0±0.1Å, 3.3±0.1Å, 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 4.25±0.1Å, 5.6±0.2Å, 6.0±0.2Å, 6.4±0.2Å, 10.0±0.3Å, and 11.2±0.3Å, respectively.

14. The method of selectively removing carbon monoxide according to claim 12, characterized in that said crystalline silicate exhibits the highest to the fifteenth highest peaks in a powder X-ray diffraction using a CuKα ray in the lattice spacing of 3.0±0.1Å, 3.05±0.1Å, 3.3±0.1Å, 3.65±0.1Å, 3.75±0.1Å, 3.85±0.1Å, 4.25±0.1Å, 4.6±0.1Å, 5.6±0.2Å, 5.7±0.2Å, 6.0±0.2Å, 6.4±0.2Å, 6.7±0.2Å, 10.0±0.3Å, and 11.2±0.3Å, respectively.

15. The method of selectively removing carbon monoxide according to claim 12, characterized in that said active metal consists of at least one metal selected from the group consisting of Pt, Pd, Ru, Rh and Ir.

16. The method of selectively removing carbon monoxide according to claim 12, characterized in that the temperature of said gaseous mixture falls within a range of between 50°C and 280°C when said gaseous mixture is introduced into said catalyst bed.

17. The method of selectively removing carbon monoxide according to claim 12, characterized in that the CO concentration of said gaseous mixture is not higher than 4%.


CATALYST LAYER FOR SELECTIVE OXIDATION OF CO UNDER HIGH TEMPERATURES 1
CATALYST LAYER FOR SELECTIVE OXIDATION OF CO UNDER LOW TEMPERATURES 2
SAMPLE GAS (CO, CO_2, H_2O, O_2, H_2)
REFINED GAS (CO_2, H_2, H_2O)
CATALYST BED 3

FIGURE

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 1826

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	EP 0 955 351 A (TOYOTA JIDOSHA KK) 10 November 1999 (1999-11-10) * the whole document *	1-11	C01B3/58
X	WO 93 19005 A (INTERNATIONAL FUEL CELLS CORP.) 30 September 1993 (1993-09-30)	1,8	
A	* page 13, line 23 - page 14, line 8 *	2-7,9-17	
A,D	EP 0 642 827 A (MITSUBISHI JUKOGYO KK) 15 March 1995 (1995-03-15)		

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 September 2000	Bogaerts, M

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14-09-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 955351 A	10-11-1999	JP 11310402 A	09-11-1999
WO 9319005 A	30-09-1993	US 6010675 A	04-01-2000
		DE 69325092 D	01-07-1999
		DE 69325092 T	30-09-1999
		EP 0631564 A	04-01-1995
		EP 0873967 A	28-10-1998
		US 5330727 A	19-07-1994
EP 642827 A	15-03-1995	JP 6296870 A	25-10-1994
		JP 7088378 A	04-04-1995
		DE 69409891 D	04-06-1998
		DE 69409891 T	10-09-1998
		WO 9419103 A	01-09-1994
		US 5677254 A	14-10-1997

EPO FORM P0459

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